

TIME-RESOLVED DETERMINATION OF INDOOR - OUTDOOR CONCENTRATION RELATIONSHIPS FOR PM_{2.5} NITRATE, SULFATE AND CARBON

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Keywords: Indoor Aerosols, PM_{2.5}, Nitrate

INTRODUCTION

Human health effects form the basis for the regulation of outdoor particulate matter, yet time activity studies show that most people, including children, spend the majority of their time indoors. Knowledge of indoor concentrations of particles of outdoor origin is needed to evaluate human exposure, especially for particles with diameters below 2.5 μm , called PM_{2.5}, that are readily transported indoors. This paper examines the indoor concentrations for PM_{2.5} aerosols of outdoor origin through chemically- and time-resolved measurements in an unoccupied house.

METHODS

Measurements were made in an unoccupied, three-bedroom, single-story home (134 m²) located in Clovis, California, a residential suburb bordering the city of Fresno. Concentrations of indoor and outdoor nitrate, sulfate and carbon were measured simultaneously with 10-minute time resolution using the integrated collection and vaporization cell. Black carbon was measured with 20-min time resolution by attenuation of light through a particle deposit on a quartz fiber filter. Indoor and outdoor vapor-phase ammonia and nitric acid were measured alternately, with 30-min time resolution each, using an automated on-line ion chromatograph system. Infiltration rates were determined using continuously released SF₆ tracer gas measured by a photoacoustic analyzer. Temperature and relative humidity were measured both inside and outside. Experiments were conducted during three intensive measurement periods; October 9-23, 2000, December 11-19, 2000 and January 16-23, 2001. The forced-air heating/cooling system and a ventilation fan were used to provide changes in the indoor/outdoor temperature differential and air exchange rates.

Penetration efficiency and indoor losses were evaluated using a physical mass balance equation. To allow for non steady-state conditions, the mass balance equation was solved using a 'forward-marching' scheme with time steps corresponding to the measurement interval of 10 min. The outdoor concentrations and infiltration rates entered into the model as a time-series of measurements. A constant deposition loss rate and penetration factor were determined by minimizing the squared relative errors summed over time, where the squared relative error is defined as the square of the difference between the measured and modeled indoor concentration divided by the measured concentration.

RESULTS AND DISCUSSION

It was found that the indoor - outdoor concentrations relationships were different for different chemical constituents. Specifically, indoor nitrate concentrations were much lower with respect to outdoors than were sulfate. By contrast, indoor ammonia levels were often higher indoors than outdoors. Indoor nitric acid concentrations were low to undetectable. Example data in Figure 1 correspond to four different house conditions as shown. The outdoor concentrations of gaseous ammonia (NH₃) and particulate nitrate

(NO_3^-) are correlated, particularly on Jan 20th. From noon on January 19th to noon on Jan 20th, the indoor ammonia and indoor nitrate are anticorrelated – as the nitrate concentration decreases, the ammonia increases. This is attributed to the dissociation of particulate nitrate into ammonia and nitric acid vapor. During periods (1) and (2), the characteristic time for nitrate infiltration from outdoors was large enough to balance the amount lost to dissociation, resulting in relatively large indoor nitrate levels. The addition of heat to the house between conditions (1) and (2) is enough to cause a perceptible shift towards the gas phase. When the infiltration rate was drastically lowered between conditions (2) and (3), much of the aerosol nitrate dissociated, resulting in large indoor ammonia levels. Indoor nitric acid remained low, apparently because the nitric acid was more readily lost to surfaces than was the ammonia gas.

The mass balance model was applied over an 8-day period from January 16-23. Model results gave penetration factors for sulfate and carbon of 0.95 and 1.0 respectively, as expected for submicrometer particles. Indoor loss rate for $\text{PM}_{2.5}$ sulfate was 0.2 h^{-1} , consistent with that expected for a conserved, submicron particles. In contrast, the indoor loss rates derived from the model were 1.3 h^{-1} for total carbon, and 2.6 h^{-1} for nitrate. Volatilization appears to account for a significant portion of the difference in penetration and deposition loss rates between nitrate and sulfate particles, and may also play a role for carbonaceous aerosols.

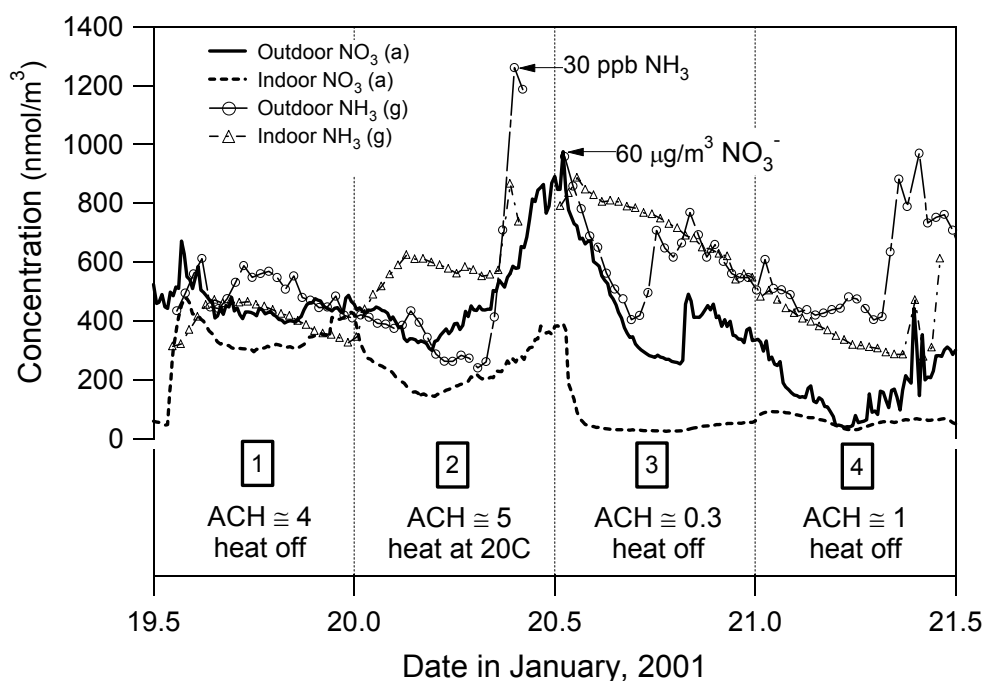


Figure 2. High time resolution measurements of the concentration of aerosol nitrate (NO_3) and gaseous ammonia (NH_3) measured outside and inside the residence during four periods with air changes per hour (ACH) and heating conditions as indicated.

ACKNOWLEDGEMENTS

This research was supported by the Assistant Secretary for Fossil Energy, Office of Natural Gas and Petroleum Technology through the National Petroleum Technology Office under U.S. Department of Energy Contract No. DE-AC03-76SF00098, and by the Western States Petroleum Association.